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Even with the recent interest in synthesis gas chemistry, the mechanisms of the various reactions and the role the catalyst plays has yet to be unequivocally established. A review of the research work carried out to elucidate the reaction mechanisms does not yield consistent conclusions in spite of the great efforts of many investigators and the use of many different scientific tools. A comparison of reaction results does not make it probable to assume basically different reaction mechanisms for different catalysts. The subtle differences noted should show greater potential for interpretation but present theories fall short of providing a unified picture capable of explaining or predicting catalyst behavior.

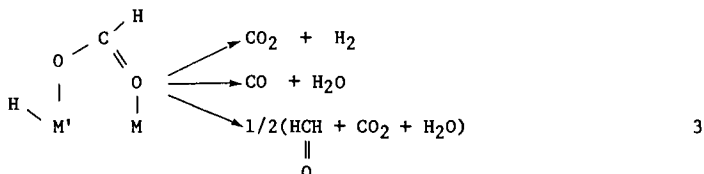
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$$\text{M} + \text{CO} + \text{H}_2 \longrightarrow \begin{array}{c} \text{C} = \text{O} \\ | \quad | \\ \text{M} \quad \text{M} \end{array} \longrightarrow \begin{array}{c} \text{O} = \text{CH}_2 \\ | \\ \text{M} \cdot \end{array} \begin{array}{l} \nearrow \text{methane} \\ \longrightarrow \text{methanol} \\ \searrow \text{hydrocarbons} \end{array} \quad 2$$

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This mechanism which integrates features of the carbide and carbenol intermediate theories⁽²⁾ has been successful in developing a new series of highly active Fischer-Tropsch (F-T) catalysts.

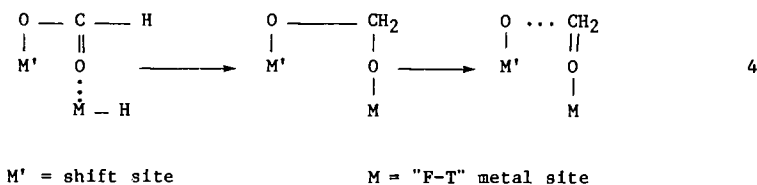
The reversibility between reduced and various oxidized states of the catalyst is an essential feature for catalyst activity in the Kolbel-Engelhardt (K-E) synthesis.⁽³⁾ Active catalysis demands some sites which promote water-gas shift activity and other sites which generate F-T intermediates. It seemed probable to us that the interaction of the water-gas shift intermediates with F-T active metal sites could explain experimental observations.

Spectroscopic studies of zinc oxide, magnesia, alumina, and iron-chromia catalysts suggest that the water-gas shift reaction proceeds through surface metal formate species.⁽⁴⁾ Other work on the decomposition of metal formates is also revealing. Their decomposition is thought to need vacant sites to occur and is enhanced by the presence of foreign metal ions.⁽⁵⁾ A bicoordinated structure can be visualized which reacts by one of three pathways.



In such decompositions, most interest in the literature has focussed upon the dehydrogenation and dehydration reactions but the minor reaction which leads to the formation of formaldehyde became the center of our attention. Although little data on this byproduct and other organics are available and little is known about the mechanism involved, appreciable amounts (~10%) of formaldehyde are formed in formic acid decompositions catalyzed by thoria, alumina, and zinc oxide.⁽⁶⁾

Mechanistic studies at Brookhaven National Laboratory (BNL) indicate that the water-gas shift formate intermediate may be the important transfer agent in the Kolbel-Engelhardt synthesis, generating the surface oxymethylene intermediate on a separate "F-T" metal site.⁽⁷⁾



As described for the F-T reaction the metal site will determine the eventual product character and distribution (Table 1) and may explain the promoting effects of alkali metals in F-T catalysis, i.e., enhanced formate formation.

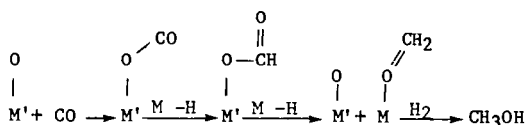
Table 1
The Use of Various Metals for the Hydrogenation of Zinc Formate

M	t _{CH₃OH}	t _{C_xH_y}
Cu/ZnO	11.7	trace
Pt/Al ₂ O ₃	11.5	trace
Pd/Al ₂ O ₃	22.6	0.1
Ni/SiO ₂	trace	8.9
Co/SiO ₂	0.1	14.8
Fe/Al ₂ O ₃	trace	2.4

water as solvent, 500 psi, H₂, 245°C, t = mole prod/mol M'

The link between metal and metal oxide catalyzed reaction of carbon monoxide are also tied to the formate transfer reaction. (In general metal oxide syngas reactions proceed via similar reaction path with methanol as the main product.)

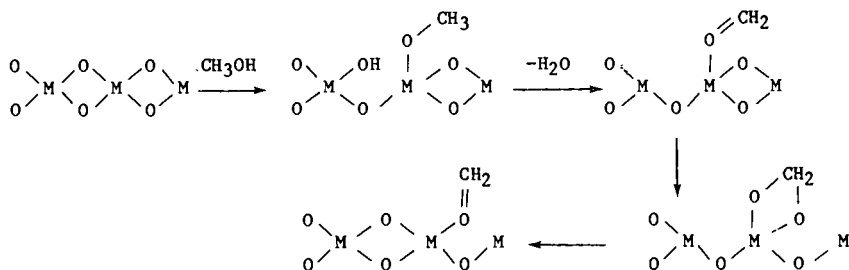
The formaldehyde-formate relationship leads to a plausible mechanism for the formation of methanol from synthesis gas. In fact, the high yield of formaldehyde (~25%) from the decomposition of zinc formate was actually considered as a commercial synthetic preparation, but was never realized. However, the reduction of the surface formaldehyde (oxymethylene) so produced was likely the cornerstone of the earliest methanol synthesis.



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As can be seen from this hypothesis, each of the metal centers in a methanol catalyst will have a particular function. One metal can be thought of as a formate center, the other as a hydrogenating center. This description of the role of formate has been used at BNL to design new K-E and methanol catalysts.

Finally, the oxymethylene species may also be involved in the initial hydrocarbons formed from methanol over non-reducible oxide catalysts. This would include products derived in the isosynthesis⁽²⁾ as well as the zeolite controlled methanol conversions.⁽⁸⁾ In both chemistries the formation of a carbenoid species from methanol seems likely. This species may be an oxymethylene formed on an acid site. As mentioned earlier, the oxide surface would allow mobility of the carbene (eq.6) and reaction with itself or other methanol molecules would be expected to yield ethylene and dimethyl ether respectively. Carbene addition to the double bond of formed olefins can also occur. This explanation is consistent with recent deuterated water observations in the conversion of methanol to ethylene⁽⁹⁾ and is in accord with the mechanistic findings of Chang.⁽⁸⁾



In summary, we have proposed that a common intermediate may be involved in many synthesis gas and related conversions. This oxymethylene moiety can be derived directly from carbon monoxide and hydrogen over a metal catalyst or indirectly from a formate intermediate in reaction involving steam or on metal oxide surfaces. We believe that the oxymethylene species symbolizes the link between these chemistries and the potential route to developing new synthesis gas catalyst systems.

References

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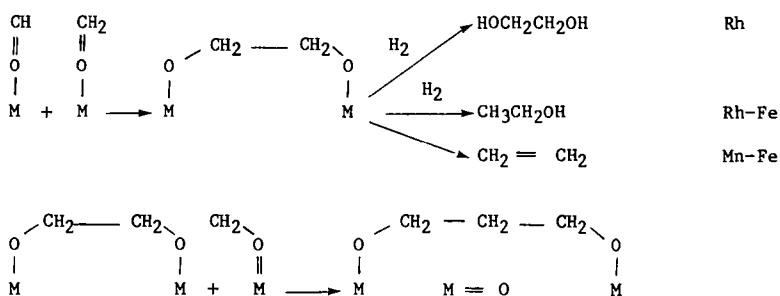
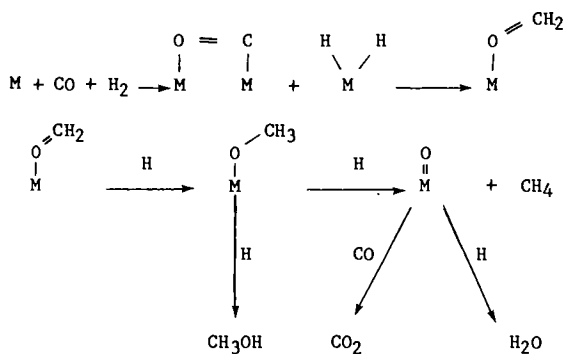


Figure 1. The oxide mechanism.(1)